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[54] 发明名称 粉煤灰的处理方法

[57] 摘要

本发明是一种处理粉煤灰的方法，用于水泥和砼中，它的工艺步骤：原材料及各占总重量的比例为 CaO 占 10－25%，石膏(以 SO3 计)占 2.5－10%，粉煤灰占 65－87.5%，沸石占 0－5%；加水充分的拌和均匀；制成一定大小的坯，常温养护；加温至 700℃－900℃；冷却成产品。优点：通过适当水通化，合适升温速度煅烧，形成结晶度差，分散度高，矿物间粘结力小及易粉磨的混合体，和水泥熟料一起粉磨或粉磨以后代替部分水泥制砼，可以促进水泥水化，并能改善水化矿物性能。

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1、处理粉煤灰的方法，其特征是工艺步骤分（1）原材料及其配比，含 $Ca(OH)_2$ 的工业废渣乙炔气渣、CaO 或 $Ca(OH)_2$ 在内的材料；含有水或无水硫酸钙、磷石膏或柠檬酸石膏；热电厂湿排或干排粉煤灰；它们各占其总重量的比例如下：以 CaO 计配入量占 10-25%，石膏以 SO_3 计配入量占 2.5-10%，粉煤灰占 65-87.5%，（2）加入占上述原材料总量的 30%的水拌和均匀，（3）制成（6—10）cm×（8—14）cm（30—50）cm 的坯，自然养护，（4）在窑内燃烧加温，用 10—20 小时将窑内的温度升至 500℃左右，然后再用 2—6 小时将窑内的温度升至 700℃-900℃，立即停止加温，（5）冷却，成品。

粉煤灰的处理方法

本发明涉及的是一种对粉煤灰的处理方法，处理后的粉煤灰可用于水泥和砼中，它属于建筑材料生产水泥原料的技术领域。

现有技术，如 CN 1165792，其说明书中称：它是一种以提高粉煤灰的活性，使之加快与氢氧化钙的反应速度而成为水泥混合材，其中的原材料半水石膏限定为 1—4%，生产工艺中采用压制成型工艺，煅烧后需 2—4 小时的保温，块料的大小呈砖型，形成的成品对水泥水化速度加快有影响，并且不可能形成含有硅酸根水化钙矾石固溶体，从而对水泥早期强度的发展有一定的影响。

本发明的目的在于针对上述存在的缺陷，提出一种新的用于水泥和砼中的粉煤灰处理方法，原料可以完全采用工业废渣，并不产生二次污染，成品可有效提高水泥胶凝性能和水泥石的稳定性以及水泥石强度，还可以加速水泥的早期水化速度，从而提高水泥早期强度，并保证后期强度发展。

本发明的技术解决方案：工艺步骤分（1）原材料及其配比，含 $Ca(OH)_2$ 的工业废渣如乙炔气渣、CaO 或 $Ca(OH)_2$ 在内的材料；含有水或无水硫酸钙、磷石膏或柠檬酸石膏等化学石膏；热电厂湿排或干排粉煤灰；有塑性的软质沸石。它们各占其总重量的比例如下：以 CaO 计并包含其它材料代入的 CaO 占 10-25%，石膏以 SO_3 计,并包含其它材料代入的 SO_3 占 2.5-10%，粉煤灰占 65-87.5%，具有塑性的软质沸石占 0—5%，（2）加入占上述原材料总量的 30%的水拌和均匀，（3）制成（6—10）cm×（8—14）cm（30—50）cm 的坯，自然养护，（4)在窑内燃烧加温,用 10-20 小时将窑内的温度升至 500℃左右，然后再用 2--6 小时将窑内的温度升至 700℃-900℃，立即停止加温，（5）冷却成品（处理后的粉煤灰产品）。

本发明的优点：处理后的粉煤灰产品中形成了分散度高的无水矿物和少量还含水矿物，它在水泥中能和钙的相互作用速度加快，

产生较好的胶凝性，并且分散度越高作用效果就越佳。因此，处理后的粉煤灰可提高水泥胶凝性能。

处理后的粉煤灰产品包含有细硅粉特性，适量的硅粉在水泥中，可以减少水泥石中羟基钙石的含量，增加水化硅酸钙的成分，提高水泥石的稳定性。

处理后的粉煤灰产品中含有部分脱了水的水化过的矿物，由于煅烧温度较低，这些矿物及新形成的矿物结晶度比较差，遇水很快复原，形成水化小晶体，处理粉煤灰中还有未完全失掉水的水化矿物，粉磨分散到水泥中也形成小晶体，这些小晶体在水泥水化中就要不断发育长大，这种就诱导水泥熟料粒子水化，所以处理后的粉煤灰可以加速水泥水化，

处理后的粉煤灰产品在可能的情况下，是尽量减少钙的用量，其钙硅比一般在 1.0 以下。处理后的粉煤灰在水泥中硅铝活性之高，分散度之大，是直接用粉磨等手段难以达到的，并且在处理粉煤灰中含有适当的硫酸盐存在，这就使得含处理后的粉煤灰产品的水泥形成的水化矿物更合理，结果使水泥石强度提高，更富有耐久性。

实施例 1 （原料总重量为 1000 公斤）

用适当的处理后的粉煤灰产品代替熟料粉磨水泥，以同样的粉磨条件来比较，加处理后的粉煤灰的水泥，同期的抗压和抗折强度能大于纯熟料加石膏磨出的水泥。表一数据就是很好的例子。粉煤灰占重量的 65%，磷石膏占重量的 12%，电石渣(乙炔气渣) 占重量的 18%，软沸石占重量的 5%，再加入占上述原材料总量的 30%的水拌和均匀，制成 10cm×12cm×40cm 的坯，自然养护（防晒防大雨淋），在窑中用 15 小时左右烧至窑内温度达 880℃即冷却。我们从表一强度发展的情况看，用处理后的粉煤灰的水泥，7 天以后强度增长率高于由熟料加石膏粉磨出来的水泥，由此可见，加处理粉煤灰的水泥强度增长潜力是比较大的。

实施例 2（原料总重量为 1000 公斤）

处理后的粉煤灰产品在实验室做出的结果是比较理想的，在大生产中也有较好的效果。表二（处理粉煤灰生产：粉煤灰占重量的 70%，

柠檬酸石膏占重量的 10%，电石渣占重量的 20%，再加入占上述原材料总量的 30%的水拌和均匀，制成 8 厘米×16 厘米×30 厘米坯经 18 小时升温至 900℃就冷却。与某厂实际生产情况比较，该厂原来生产的 425 号粉煤灰硅酸盐水泥，作的熟料是 68%左右，而用了处理后的粉煤灰产品，仅用 50%的熟料，从表中连续叁个编号平均强度看，仅用 50%的熟料强度值高于用 68%熟料值。因此可以结论，用部分处理后的粉煤灰作为混合材生产水泥是有效果的。

实施例 3：既然处理后的粉煤灰和熟料一起粉磨水泥效果是好的，则粉磨后在未加处理后的粉煤灰水泥中代替部分水泥当然也是有好的效果，至少说用适量处理后的粉煤灰代替水泥，砂浆强度能保持不变。表三（所用处理粉煤灰工艺同上）所列数据就是用 15%经处理粉磨的粉煤灰代替水泥试验情况比较，从表可得，用 15%经粉磨的处理粉煤灰代替水泥能使水泥原来强度保持不变，并能适当增加。

表一，处理后的粉煤灰（处理灰）在水泥中有关物理性能

编号	熟料%	天然二水石膏%	处理灰%	细度%	初凝时分	终凝时分	抗压强度(Mpa)			抗折强度(MPa)		
							3天	7天	28天	3天	7天	28天
D1	96	4	-	4.6	1:40	2:35	34.3	49.1	57.8	6.3	7.1	8.4
D2	76	4	20	3.1	1:40	3:10	40.1	54.6	63.8	6.6	7.9	9.1
D3	57	3	40	3.0	1:50	3:25	33.6	45.4	57.5	5.4	6.9	8.4

表二，处理后的粉煤灰（处理灰）在水泥大生产中应用物理性能情况

编号	熟料%	天然二水石	粉煤灰%	处理灰%	台产吨/小时	细度%	初凝时分	终凝时分	抗压强度(MPa)	抗折强度(Mpa)

									3天	7天	28天	3天	7天	28天
A-40-43	68	4	28	-	14	4.1	3:10	4:20	26.7	36.1	50.2	4.8	5.9	7.6
A-44-46	50	3	32	15	16	4.1	2:20	3:30	29.8	40.8	55.8	5.4	6.6	8.4

表三，用15%处理后的粉煤灰（处理灰）代替水泥砂浆强度比较

编号	普通水泥%	矿渣水泥%	混合水泥%	粉磨处理灰%	抗压强度(MPA)			抗折强度(MPA)		
					3天	7天	28天	3天	7天	28天
D68	100	-	-	-	28.4	38.6	52.6	5.0	6.1	7.6
D69	85	-	-	15	29.6	39.8	54.1	5.2	6.4	7.8
D70	-	100	-	-	27.8	38.9	54.0	4.8	6.0	7.8
D71	-	85	-	15	28.4	39.6	54.9	5.0	6.2	8.4
D72	-	-	100	-	28.2	38.6	52.8	4.9	6.1	7.5
D73	-	-	85	15	28.3	38.5	53.0	4.9	6.0	7.5

粉煤灰包括劣质粉煤灰经处理后在水泥和砼中应用效果是好的，可以说为开发粉煤灰在水泥中应用又开创了一条新的路子。

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[54] Title: Method for processing coal fly ash

[57] ABSTRACT

The invention discloses a method for processing coal fly ash used in cement and concrete. The process comprises the steps of: raw material proportioning, with 10-25% of CaO, 2.5-10% of gypsum (by weight of SO_3), 65-87.5% of coal fly ash and 0-5% of zeolite, based on the total weight of the raw materials; adding in water and stirring homogeneously; shaping the raw materials into a blank in a certain size and curing at normal temperature; heating the temperature to 700-900 degree Celsius; and cooling to obtain a finished product, which is a mixture with poor degree of crystallization, high degree of dispersion, small adhesion between minerals and ease of grinding. It may replace partial cement after being ground, or it may be ground together with cement clinker. It can facilitate cement hydration and improve the performance of hydrated minerals.

CLAIMS

1. A method for processing coal fly ash, characterized in that the process comprises the steps of:

   1) proportioning raw materials, which comprise $Ca(OH)_2$ contained industrial residues such as acetylene residue, CaO or $Ca(OH)_2$; hydrated or non-hydrated calcium sulfate, phosphogypsum or citric acid gypsum; coal fly ash from wet or dry discharge of thermal power plant; with respective percentages based on the total weight of the raw materials as follows: 10-25% of CaO, 2.5-10% of gypsum (by weight of SO_3), and 65-87.5% of coal fly ash;

   2) adding in 30% of water based on the total weight of the raw materials and stirring homogeneously;

   3) shaping the raw materials into a blank having a size of (6-10)cm×(8-14)cm×(30-50)cm and curing at normal temperature;

   4) placing the blank in a kiln, heating the temperature inside the kiln to about 500 degree Celsius in 10-20 hours and further to 700-900 degree Celsius in another 2-6 hours, then immediately stopping heating;

   5) cooling to obtain a finished product.

SPECIFICATION

Method for processing coal fly ash

The invention relates to a method for processing coal fly ash. The processed coal fly ash can be used in cement or concrete. The invention belongs to the technical filed of production of cement raw material for construction.

As a prior art, Chinese patent application CN 1165792A discloses a process of enhancing the activity of coal fly ash and accelerating its reaction with calcium hydroxide to form a cement mixture, in which the raw material of semi-hydrated gypsum is limited to 1-4%. The process of press molding is adopted, with the temperature being hold for 2 to 4 hours after calcining. The lump material is in a size of a brick. The finished product has an effect on rapidity of the cement hydration without forming a solid solution containing hydrated ettringite silicate, thus impairing to a certain extent the growth of cement strength at its early stage.

Aiming at the disadvantages identified above, the purpose of this invention is to provide a new method for processing coal fly ash used in cement and concrete, the raw material of which can completely be industrial waste residue, thus avoiding secondary pollution. The finished product can effectively improve the gelation properties of cement as well as the stability and strength of hardened cement, and further increase the rapidity of cement hydration at early stage, resulting in enhanced cement strength at early stage and ensuring the strength growth at later stages.

The technical solution of this invention comprises the steps of:

1) proportioning raw materials, which comprise $Ca(OH)_2$ contained industrial residues such as acetylene residue, CaO or $Ca(OH)_2$; hydrated or non-hydrated calcium sulfate, phosphogypsum or citric acid gypsum; coal fly ash from wet or dry discharge of thermal power plant; and soft plastic zeolite, with respective percentages based on the total weight of the raw materials as follows: 10-25% of CaO (including the CaO brought in with other materials), 2.5-10% of gypsum (by weight of SO_3, including the SO_3 brought in with other materials), 65-87.5% of coal fly ash, and 0-5% of soft plastic zeolite;

2) adding in 30% of water based on the total weight of the raw materials and stirring homogeneously;

3) shaping the raw materials into a blank having a size of (6-10)cm×(8-14)cm×(30-50)cm and curing at normal temperature;

4) placing the blank in a kiln, heating the temperature inside the kiln to about 500 degree Celsius in 10-20 hours and further to 700-900 degree Celsius in another 2-6 hours, then immediately stopping heating;

5) cooling to obtain a finished product (i.e. processed coal fly ash).

As an advantage of this invention, non-hydrated minerals having a high degree of dispersion and a small amount of hydrated minerals are formed in the product of processed coal fly ash, resulting in faster reaction with calcium in cement and improved gelation properties. The higher the degree of dispersion, the better the reaction effect. Therefore, the processed coal fly ash can improve the

gelation properties of cement.

The processed coal fly ash is equipped with the properties of fine silicon powder. An appropriate amount of fine silicon powder in the cement can help to reduce the content of hydroxyl calcium, increase the ingredient of hydrated calcium silicate, and enhance the stability of hardened cement.

The processed coal fly ash contains hydrated minerals which have been partly dehydrated. Calcined at a lower temperature, these minerals and the newly formed minerals have a poor crystallization degree, allowing them to restore to their original state when they get in touch with water, and forming hydrated tiny crystals. In addition, the processed coal fly ash further contains hydrated minerals not completely dehydrated, which can also form tiny crystals after being ground and dispersed in cement. The tiny crystals grow constantly during the hydration of cement, thus facilitating the hydration of cement clinker particles and resulting in accelerated rapidity of cement hydration.

Where possible, the processed coal fly ash minimizes the use of calcium, with a calcium/silicon ratio of 1.0 or less. The processed coal fly ash in cement has a high activity of silicon and aluminum and a high degree of dispersion, which cannot be achieved directly through means such as pulverization. Besides, due to the existence of an appropriate amount of sulfate in the process, the cement containing finished coal fly ash can form a sound hydrated mineral, resulting in improved strength of hardened cement and excellent durability.

Embodiment 1 (total weight of raw material of 1000 kg)
An appropriate amount of processed coal fly ash is used to replace clinker in grinding cement. Compared under the same grinding conditions, the cement using the processed coal fly ash has better compressive strength and flexural strength than the cement obtained through grinding of pure clinker and gypsum at a same stage. Data shown in Table 1 gives a good example. To produce a blank in a size of 10cm × 12cm × 40cm, 65 wt% of coal fly ash, 12 wt% of phosphogypsum, 18 wt% of acetylene residue, 5 wt% of soft plastic zeolite are mixed with 30% of water based on the total weight of the above raw materials and homogeneously stirred. The blank is cured at normal temperature (to avoid insolation and drenching), which is further heated in the kiln for about 15 hours before the temperature inside the kiln reaches 800 degree Celsius and the blank starts to be cooled. As indicated by the growth of strength shown in Table 1, after 7 days, the cement using the processed coal fly ash exhibits a higher growth rate of strength than the cement obtained through grinding of pure clinker and gypsum. In this way, the cement using the processed coal fly ash has a greater potential of strength growth.

Embodiment 2 (total weight of raw material of 1000 kg)
The product of processed coal fly ash exhibits an ideal performance not only in the laboratories, but also in mass production, as shown in Table 2. To produce a blank in a size of 8cm × 16cm × 30cm, 70 wt% of coal fly ash, 10 wt% of citric acid gypsum and 20 wt% of acetylene residue are mixed with 30% of water based on the total weight of the above raw materials and homogeneously stirred. The blank is heated for 18 hours before the temperature reaches 900

degree Celsius and the blank starts to be cooled. Comparison with the actual production of a company shows that the original 425# coal fly ash silicate cement consumes about 68% of clinker, while the clinker consumption in its new cement product using the processed coal fly ash is merely 50%. As indicated in the table, the strength with 50% of clinker is greater than that with 68%. Therefore, it is concluded that partial use of the processed coal fly ash in cement can generate good effects

Embodiment 3

Now that the grinding of processed coal fly ash and clinker for cement production can generate good effects, the addition of the processed coal fly ash after grinding in unprocessed coal fly ash cement to replace part of the cement will be effective as well. The replacement of an appropriate amount of processed coal fly ash to the cement can at least maintain the mortar strength. Data in Table 3 (with ditto process of coal fly ash) compares the testing results after 15% of the cement is replaced by the ground processed coal fly ash. It is concluded that the cement strength can be maintained, or even improved, after 15% of the cement is replaced by the ground processed coal fly ash.

Table 1 Physical performance of processed coal fly ash in cement

No	% of Clinker	% of natural dihydrated gypsum	% of processed coal fly ash	% of fineness	Initial set time	Final set time	Compressive Strength (Mpa)			Flexural Strength (Mpa)		
							3 Days	7 Days	28 Days	3 Days	7 Days	28 Days
D1	96	4	-	4.6	1:40	2:35	34.3	49.1	57.8	6.3	7.1	8.4
D2	76	4	20	3.1	1:40	3:10	40.1	54.6	63.8	6.6	7.9	9.1
D3	57	3	40	3.0	1:40	3:25	33.6	45.4	57.5	5.4	6.9	8.4

Table 2 Physical performance of processed coal fly ash in mass cement production

No	% of Clinker	% of natural dihydrated gypsum	% of coal fly ash	% of processed coal fly ash	Production ton per hour	% of fineness	Initial set time	Final set time	Compressive Strength (Mpa)			Flexural Strength (Mpa)		
									3 Days	7 Days	28 Days	3 Days	7 Days	28 Days

A-40 -43	68	4	28	-	14	4.1	3:10	4:20	26.7	36.1	50.2	4.8	5.9	7.6
A-44 -46	50	3	32	15	16	4.1	2:20	3:30	29.8	40.8	55.8	5.4	6.6	8.4

Table 3 Physical properties of treated coal fly ash in cement

No	% of regular cement	% of slag cement	% of mixed cement	% of processed coal fly ash	Compressive Strength (Mpa)			Flexural Strength (Mpa)		
					3 Days	7 Days	28 Days	3 Days	7 Days	28 Days
D68	100	-	-	-	28.4	38.6	52.6	5.0	6.1	7.6
D69	85	-	-	15	29.6	39.8	54.1	5.2	6.4	7.8
D70	-	100	-	-	27.8	38.9	54.0	4.8	6.0	7.8
D71	-	85	-	15	28.4	39.6	54.9	5.0	6.2	8.4
D72	-	-	100	-	28.2	38.6	52.8	4.9	6.1	7.5
D73	-	-	85	15	28.3	38.5	53.0	4.9	6.0	7.5

The good effects identified above demonstrate that this invention has developed a new way of applying coal fly ash in cement.